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He is fed twice a day by an old woman, at low water, with salmon caught in the preceding year. At the end of the first month he deposits his clothing in the woods, and then he is allowed to sit in a corner of the house, but must not speak to the other people. A separate door is cut, as he is not allowed to use the house door. Before he leaves the house for the first time, he must approach the door three times and return without going out. Then he is allowed to leave the house. After four months he may speak to other people. After ten months his hair is cut short, and the end of the year is the end of the mourning period. After the death of a chief, his son gives a great festival, in which he takes the office and name of his father. At first, four mourning songs are sung, which have a slow movement, and then the son of the chief stands up, holding the copper-plate in his hand and saying, "Don't mourn any more. I will be chief. I take the name of my father."

The marriage ceremonies of the Kwakiutl tribes are very remarkable. The dowry of the bride consists of bracelets made of beaver toes, copperplates, so called "button-blankets," and the Gyiserstal. The latter is a board, the front of which is set with sea-otter teeth. It is intended to represent the human lower jaw; and the meaning is, that the bride will have to speak or be silent, as her husband may desire. Before and after the marriage, the son-in-law gives many presents to his wife's father. If the woman intends to return to her parents, her father must repay all he has received from his son-in-law. This is done frequently, in order to give an opportunity to the father-in-law to show his liberality and wealth. As soon as he has paid the husband, the latter repurchases his wife. The use of the Gyiserstal is very limited. I found it only among the Kwakiutl proper and Nimkish.

I do not intend to describe the houses, the hunting and fishing, and industries of all these tribes, neither will I attempt to discuss the character of the art products of the different groups. I have endeavored to show in my remarks that the culture of the Northwest American tribes, which to the superficial observer seems so uniform, originates from many different sources, and that only a thorough knowledge of the languages, folklore, and customs of these tribes and their neighbors will enable us to trace at least part of their obscure history.

Electrolysis of Lead Solutions. Determination of Boric Acid. Dihalogen Derivatives of Salicylic Acid. Barite. By Edgar F. Smith.

(Read before the American Philosophical Society, Nov. 18th, 1887.)

The following is a report of work prosecuted in the laboratory of Wittenberg College, Springfield, Ohio, during the past year, partly by myself and partly by students under my supervision:

I. Electrolysis of Lead Solutions.

Lead is one of the metals which has given analysts considerable trouble

to estimate electrolytically; consequently, many suggestions have been offered, as to the best course to pursue in determining it in this manner. In this note I purpose giving some results obtained by using an alkaline solution of lead containing a phosphate. Employing a lead solution with an unknown quantity of lead, I took from it, 5 c.c., to which I added an excess of disodium phosphate, dissolving the precipitate formed in sodium hydroxide, then subjected the liquid to the action of a current derived from three small Grove cells, for a period of two hours, after which the action was interrupted; the deposit of metallic lead was washed with water, alcohol and ether, then carefully dried and weighed. In this manner I obtained .0105 grs. Pb. A second experiment conducted under like conditions gave a similar result. With 10 c.c. of the lead solution the following amounts of lead were obtained:

The same current strength was used in all these determinations, but the time varied from two to four hours. In all instances, the precipitated metal showed a regular, compact appearance.

I analyzed another lead solution of unknown strength, using, as before, sodium phosphate and hydroxide, and obtained:

$$\left. \begin{array}{c} .0225 \text{ grams} \\ .0217 \end{array} \right\} \quad \text{Pb.}$$

The current was from three small Grove cells. Time,  $3\frac{1}{2}$  hours.

Subsequently, I dissolved 8.7315 grams of lead nitrate in 250 c.c. water, and treated as follows:

- 1. One c.c. of the solution was precipitated by sodium phosphate, the precipitate dissolved in sodium hydroxide and the solution exposed to the action of a current from two Grove cells for two hours. In this way I obtained a lead deposit equal to .0215 grams Pb. The metal, after being washed with water, was dried in a current of hydrogen. This seemed necessary and was done in the following determinations:
  - 2. Same as in 1; obtained .0220 grams Pb.
  - 3. Same as in 1; obtained .0213 grams Pb.
  - 4. Same as in 1; obtained .0220 grams Pb.

The theoretical amount of lead in the electrolyzed solution was .0219 grams.

These experiments indicate that the metal can be deposited in good form from an alkaline phosphate solution, but to insure satisfactory results, great care must be exercised in the drying, as the moist metal oxidizes readily.

## II. Experiments in the Determination of Boric Acid. By E. B. Knerr.

It was observed that a considerable quantity of uranium nitrate could be added to a borax solution containing potassium ferrocyanide before the characteristic red-brown precipitate of uranium ferrocyanide appeared. This suggested the possibility of obtaining a quantitative method for the estimation of boric acid. I, therefore, dissolved 4.18 grams of uranium nitrate in one litre of water, and 1.16 grs. of well-crystallized borax in 250 c.c. water. The uranium solution was then placed in a burette and carefully added to definite portions of the borax solution until a drop of the mixture, added by means of a thin glass rod, to a drop of a concentrated potassium ferrocyanide solution, on a porcelain plate, gave a red-dish-brown color. The first distinct coloration was regarded as the final reaction. The following results were obtained:

| 1.  | 5 c.c. of | the bora | x solution | required | 8.8 c. | c. | uranium nitrate. |
|-----|-----------|----------|------------|----------|--------|----|------------------|
| 2.  | "         | "        | "          | "        | 8.9    | "  |                  |
| 3.  | "         | "        | ٠.         | "        | 8.8    | "  | "                |
| 4.  | "         | "        | 4.6        | 1.6      | 8.8    | "  | "                |
| 5.  |           | "        | "          | "        | 8.8    | "  | "                |
| 6.  | "         | 46       | "          | "        | 8.8    | "  | "                |
| 7.  | "         | "        | "          | "        | 8.8    | "  | "                |
| 8.  | "         | "        | "          | "        | 8.8    | "  |                  |
| 9.  | "         | 6.6      | 6.6        | "        | 8.8    | "  | "                |
| 10. | 10 c.c.   | "        | 66         | "        | 17.7   | "  | "                |
| 11. | "         | "        | "          | **       | 17.6   | ٠. | 4.6              |

A second uranium nitrate solution, containing 8.6267 grams nitrate in 500 c.c. of water, was standardized as above with a borax solution (containing .9051 grams borax in 250 c.c. water). The results were as follows:

```
1. 5 c.c. borax solution required 1.35 c.c. uranium nitrate.
```

| 2. | " | "   | "  | " | "" |   |
|----|---|-----|----|---|----|---|
| 3. | " | 4.6 | "  | " | "  | • |
| 4. | " | "   | ** | " | "  | • |
| 5  | " | "   | "  | " |    |   |

From this we discover that 1 c.c. of uranium solution equaled .004917 grams  $B_0O_3$ .

To test the accuracy of the method, I dissolved 1.1762 grams freshly crystallized borax in 250 c.c. of water, and titrated portions of it with the above standardized uranium solution:

| 1 | 10 | C.C. | οf | borax so | lution | required | 4.0 | ) c c | uranium solu | tion. |
|---|----|------|----|----------|--------|----------|-----|-------|--------------|-------|
|   |    |      |    |          |        |          |     |       |              |       |

| 2. | "   | • • | "   | 3.5 | " | " |
|----|-----|-----|-----|-----|---|---|
| 3. | "   | "   | "   | 3.4 | " | " |
| 4. | "   | "   | "   | 3.5 | " | " |
| 5. | "   | "   | "   | "   | " | " |
| 6. | 4.6 | "   | "   | "   | " | " |
| 7. | **  | 61  | * * | "   | " | " |
|    |     |     |     |     |   |   |

Taking 10 c.c. of the borax solution as equivalent to 3.5 c.c. of the uranium solution, we have the 250 c.c. of the borax solution equal to 85 c.c. of the uranium solution; but the 85 c.c. represent  $85 \times .004917$  grms.  $B_2O_3 = .43023$  grms.  $B_2O_3$  or 36.57%. The theoretical amount of boric acid in 1.1767 grms. borax is .43114 grs. B<sub>2</sub>O<sub>3</sub> or 36.64%.

Free acid very materially affects the results. Extremes of dilution also influenced the same to a certain degree.

I next endeavored to ascertain how ferric salts would act upon borax. At first, potassium ferrocyanide was employed as an indicator. but was later rejected. On substituting potassium sulphocyanide for it, a few drops of the same were placed in the vessel containing the borax. The first decided "blush" which came over the solution was counted as the end of the reaction. I standardized a definite amount of ferric ammonium sulphate with a definite quantity of borax, finding that one c.c. of the iron solution was equivalent to .004479 grams B<sub>2</sub>O<sub>3</sub>. I then dissolved 1.2651 grms. of borax in 250 c.c. of water, and titrated a number of portions with the standardized iron solution. The results were 36.73% B<sub>2</sub>O<sub>3</sub>, instead of 36.64% by theory.

Upon standardizing a new quantity of iron salt, instead of adding the sulphocyanide solution directly to the borax solution, a few drops of it were placed upon a porcelain plate, and as the end reaction was approached. portions of the liquid were brought in contact with the sulphocyanide by means of a glass rod. In this way the following numbers were obtained:

10 c.c. borax solution required 1.05 c.c. iron solution.

| 2.         | "  | "    | "       | **  | "    | " | " |
|------------|----|------|---------|-----|------|---|---|
| 3.         | 5  | c.c. | "       | 4.6 | 0.5  | " | " |
| 4.         | 10 | "    | **      | "   | "    | " | " |
| <b>5</b> . | 5  | "    | <b></b> | "   | 0.5  | " | " |
| 6.         | 10 | **   | 4.6     | "   | 1.05 | " | " |
| 7.         | "  | "    | "       | "   | • •  | " | " |
| 8.         | 20 | "    | "       | "   | 2.10 | " | " |
| 9.         | "  | "    | "       | "   | 4.6  | " | " |
| 10.        | 40 |      | "       | "   | 4.20 | " | " |

Thus, I found that one c.c. of the iron solution was equal to .00967 grms. B<sub>2</sub>O<sub>8</sub>.

The following tests were then made with the iron solution:

1. 2.2741 grms. borax were dissolved in 250 c.c. of water, and portions of it titrated:

> " "

. .

```
10 c.c. borax required 3.40 c.c. iron solution.
                             "
```

" This gave 36.14% B<sub>2</sub>O<sub>3</sub>; theory 36.64%.

20 "

 Six determinations were made with a solution containing 2.1490 grms. borax in 250 c.c. water.

Found 36.40% B<sub>2</sub>O<sub>3</sub>, instead of 36.64%.

- 3. With a solution containing .0865 grms. of borax, I obtained 36.89%  $\rm B_2O_3.$
- .0254 grms. borax, dissolved in water and titrated, showed 36.46%
   B<sub>2</sub>O<sub>2</sub>, instead of 36.64%.
- 5. .0104 grms. borax gave 37.50% B<sub>2</sub>O<sub>3</sub>.
- 6. .0198 grms. borax, titrated as before, gave 36.35% B<sub>2</sub>O<sub>3</sub>.

A number of determinations showed that sodium salicylate can also be advantageously employed as an indicator.

For rapid work, where approximate results are sufficient, the foregoing methods will no doubt be of service. Free acids should always be avoided.

I have also experimented with tungstic and molybdic acids in the same manner, and while the results are very promising. I prefer reserving an account of the same until the details have been fully worked out.

#### III. Dihalogen Derivatives of Salicylic Acid. By W. S. Hoskinson.

In the American Chemical Journal, Vol. viii, No. 2, Smith and Knerr described metachloriodosalicylic acid and its derivatives. Pursuing a somewhat similar line of research, I prepared a brom-chlor-acid, and an iodo-brom-salicylic acid, as well as derivatives of the same. Below I give a brief description of these new compounds.

### Brom-chlor-salicylic Acid.

## C<sub>6</sub>H<sub>9</sub> OH BrCl COOH.

To obtain this acid I used a definite quantity of metachlorsalicylic acid (m.p. 172°C.), and dissolved the same in alcohol. To this solution was gradually added a corresponding, equivalent amount of bromine; the flask in which the reaction was performed was kept cool. When the entire quantity of bromine was added, the alcoholic solution was evaporated to dryness upon a water bath. The residue was boiled with water and barium carbonate, the liquid filtered and allowed to cool. The barium salt separated in bushy needles. Its solubility in water is about 1:100. The sodium salt was prepared from the barium salt, and from it the acid was liberated by hydrochloric acid. The free acid forms small, white needles, nearly insoluble in boiling water, but soluble in alcohol. In its pure state it melts constantly at 229°C.

The barium salt [( $C_6H_2$  OH BrCl CO)<sub>2</sub> Ba + 4H<sub>2</sub>O] forms long bushy needles, soluble with difficulty in boiling water. An analysis of it gave 10.02% H<sub>2</sub>O and 21.20% Ba. The formula given requires 10.14% H<sub>2</sub>O and 21.48% Ba.

The sodium salt ( $C_6H_2$  OH BrCl COONa +  $1\frac{1}{2}$   $H_2O$ ) appears in beautiful bunches of white needles, which are very soluble in water. An

analysis showed 9.09%  $\rm\,H_2O$  and 8.25% Na; theory requires 9.89%  $\rm\,H_2O$  and 8.40% Na.

The  $calcium\ salt$  is analysis gave 7.42% Ca, while theory requires 7.39%.

The zinc salt forms small crystals, much like fish-eggs. It dissolves with difficulty in hot water. When analyzed it gave 13.91% H<sub>2</sub>O and 12.24% Zn; the theoretical figures are 14.06% H<sub>2</sub>O (5 molecules), and 11.94% Zn.

The magnesium salt does not crystallize well. It is not readily soluble, even in hot water. It contains six molecules of water of crystallization. Upon analysis I obtained 17.19% H<sub>2</sub>O and 5.33% Mg. The calculated percentages of water and magnesium are 17.03% and 4.79%.

The cadmium salt forms beautiful crystals.

The silver salt was obtained as a white precipitate insoluble in water. I employed it in preparing the methyl and ethyl esters.

Methyl Ester ( $C_6H_2$  OH BrCl CO OCH<sub>3</sub>). This was obtained by the action of methyl iodide upon the silver brom-chlor-salicylate. It forms beautiful needles, dissolving with difficulty in both alcohol and ether. It melts at  $126-127^{\circ}$  C. This ester was burned with lead chromate, and gave good results. The *ethyl ester*, also prepared, was not further studied.

The free brom-chlor acid was burned with lead chromate. The result showed 33.07% carbon and .96% H. Theory requires 33.46% C and 1.53% H.

#### Iodo-brom-salicylic Acid.

#### C<sub>6</sub>H<sub>2</sub> OH IBr COOH.

Metabrom-salicylic acid was first prepared, and then iodated by the method of Weselsky. Little heat was evolved in the reaction; sometimes this was added by means of the water-bath. When the reaction was complete the alcoholic solution was removed to an evaporating dish and run down to dryness. The residue was boiled with water and barium carbonate; from the hot filtrate the barium salt crystallized out, but it was immediately converted into the sodium salt, from which I set the acid free. The latter forms small, beautiful needles, dissolving with difficulty in hot alcoholic water. It melts at 208-209° C. A combustion of the pure acid gave 24.17% carbon and 1.30% H, instead of 24.48% C and 1.17% H.

The barium salt contains three molecules of water. It forms branched, purple-tinted needles. An analysis gave 6.48% H<sub>2</sub>O and 15.55% Ba, instead of 6.27% H<sub>2</sub>O and 15.65% Ba, as required by theory.

The *sodium salt* contains one molecule of water. It forms nodules, consisting of silky needles, very soluble in water. When analyzed it yielded 5.20% H<sub>2</sub>O and 6.08% Na; theory requires 4.70% H<sub>2</sub>O and 6.30% Na.

The calcium salt resembles the barium salt in form; it is possibly somewhat more soluble in hot water. It contains four molecules of water. Its

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analysis gave  $8.04\%~H_2O$  and 5.65%~Ca, instead of the theoretical  $8.01\%~H_2O$  and 5.53%~Ca.

The cadmium salt forms beautiful needles, readily soluble in water. Its analysis showed  $8.21\%~H_2O$  and 14.13%~Cd, instead of  $8.29\%~H_2O$  and 14.19%~Cd.

The zinc salt consists of indistinct needles, readily soluble in water. Its analysis showed the presence of five molecules of water, and 10.51% Zn.

The methyl ester crystallizes in beautiful needles, which melt at 104–105° C. By its combustion I obtained 26.23% C and 2.15% H. Its formula requires 26.86% C and 1.68% H.

The study of other mixed dihalogen derivatives of salicylic acid is being carried forward in this laboratory, the results of which will be published later.

# IV. Barite from Ludlow Falls, Miami County, Ohio. By Charles H. Ehrenfeld.

This mineral was found in the summer of 1886, the chief interest in connection with it being that it is the first time barite has been found in this locality. It is white, semi-transparent and massive, and it occurs in the Niagara limestone, associated with small crystals of pyrite, the surface of which is brown owing to oxidation. The average of four sp. gr. determinations of the barite is 4.48.

An analysis showed the following composition:

| Total             |         |
|-------------------|---------|
| CaSO <sub>4</sub> |         |
| SrSO <sub>4</sub> | 7.63 '' |
| BaSO <sub>4</sub> | 91.10%  |

CHEMICAL LABORATORY OF WITTENBERG COLLEGE, Springfield, Ohio, Nov. 8, 1887.

## Stated Meeting, December 2, 1887.

Present, 34 members.

President, Mr. FRALEY, in the Chair.

Dr. Morton W. Easton was presented to the Chair and took his seat.

Correspondence was submitted as follows: Letters acknowledging receipt of diploma from Messrs. R. N. Toppan, Cambridge, Mass.; William John Potts, Camden, New Jersey; Charles A. Oliver and Henry Reed, Philadelphia.